Multielectron atoms, the Pauli principle & periodic table

Having solved the electronic levels of the hydrogen, we can extend the results to explain the whole periodic table with inclusion of the Pauli principle and some approximation called the independent-Particle approximation (IPA) [more precisely the Hartree-Fock method]. We won't be doing the sophisticated calculations/computation, and we will be content with simple calculation

↓ see Morrison's book & the applet

and qualitative explanation.

IPA: treat each e^- independently, but take into account force/potential from the nucleus and $Z-1$ other electrons (in an averaged way).

⇒ IPA potential $U(r) = -Z_{eff}(r) \dfrac{ke^2}{r}$

① if r outside all other e^- : $U(r) = -\dfrac{ke^2}{r}$

② if r close to nucleus $r \to 0$: $U(r) = -\dfrac{kZe^2}{r}$
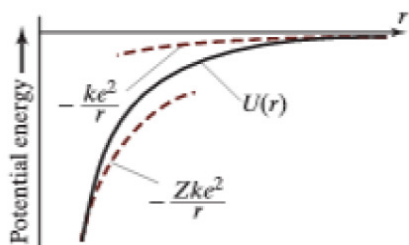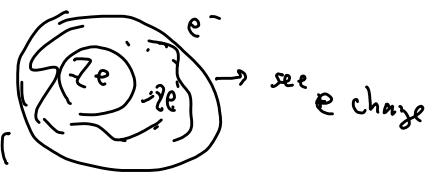
see e charge

FIGURE 10.1

The IPA potential energy $U(r)$ of an atomic electron in the field of the nucleus plus the average distribution of the other $Z-1$ electrons. As $r \to \infty$, U approaches $-ke^2/r$; as $r \to 0$, U approaches $-Zke^2/r$ as in Eq. (10.5).

With the assumption that $U(r)$ depends on r only, not on (θ, φ) ⇒ the labels for the states are the same as those for hydrogen atom

n: principle q#

l: orbital angular mom. $= 0, 1, 2, \cdots, n-1$ (?)

m: azimuthal q# $= -l$ to l

$1s, 2s, 2p$, etc.

① In the region 1s is large $U(r)$ ⟹ $Z_{eff} \approx Z$

energy of 1s $\overline{E}_{1s} \approx -Z^2 E_R$ $E_R \simeq 13.6\,eV$

② 2s & 2p degenerate for hydrogen. But with multiple electrons

2s states are lower in energy than < 2p,

as 2s orbital has more portion closer to nucleus, see larger Z_{eff}

Similarly $3s < 3p. < 3d$.
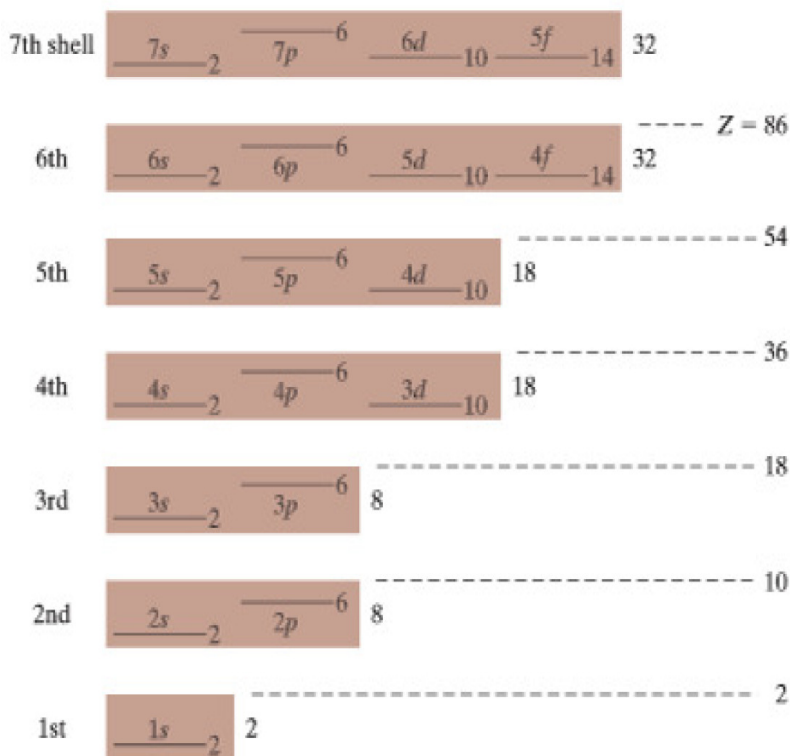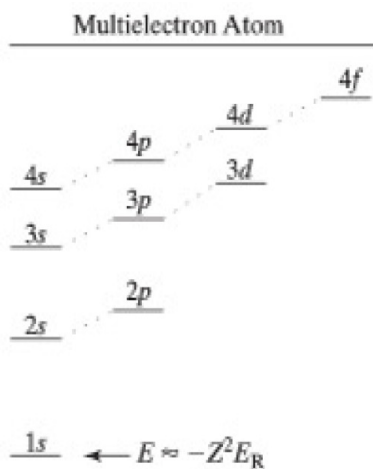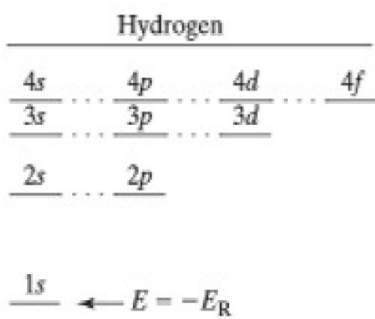
③ Size: hydrogen-like atom $r \approx n^2 a_B/Z$

(fixed n, states tend to cluster in a spatial shell)

for $n=1$. $r \approx a_B/Z$.

for layer n. $r_? \approx n^2 a_B/Z_{eff}$ $Z_{eff}^{(n)} < Z$

• clustering depends on n vs. energy levels depend on n & ℓ !

Schematic energy-level diagram showing the order in which levels are occupied


each n can accommodate

$2n^2$ electrons (including spins)

Hydrogen:
4s 4p 4d 4f
3s 3p 3d
2s 2p
1s ← $E = -E_R$

Multielectron Atom:
4f
4d
4p 3d
4s 3p
3s
2p
2s
1s ← $E \approx -Z^2 E_R$

7th shell: 7s —2 7p —6 6d —10 5f —14 32

6th: 6s —2 6p —6 5d —10 4f —14 32 ---- Z = 86

-------------- 54

5th: 5s —2 5p —6 4d —10 18

-------------- 36

4th: 4s —2 4p —6 3d —10 18

-------------- 18

3rd: 3s —2 3p —6 8

-------------- 10

2nd: 2s —2 2p —6 8

-------------- 2

1st: 1s —2 2

Fill up the levels.

It turns out that we can explain many features in the periodic table and the so-called magic # 2, 10, 18, 36, 54, 86 (in ionization energy)

Ionization energy (eV)
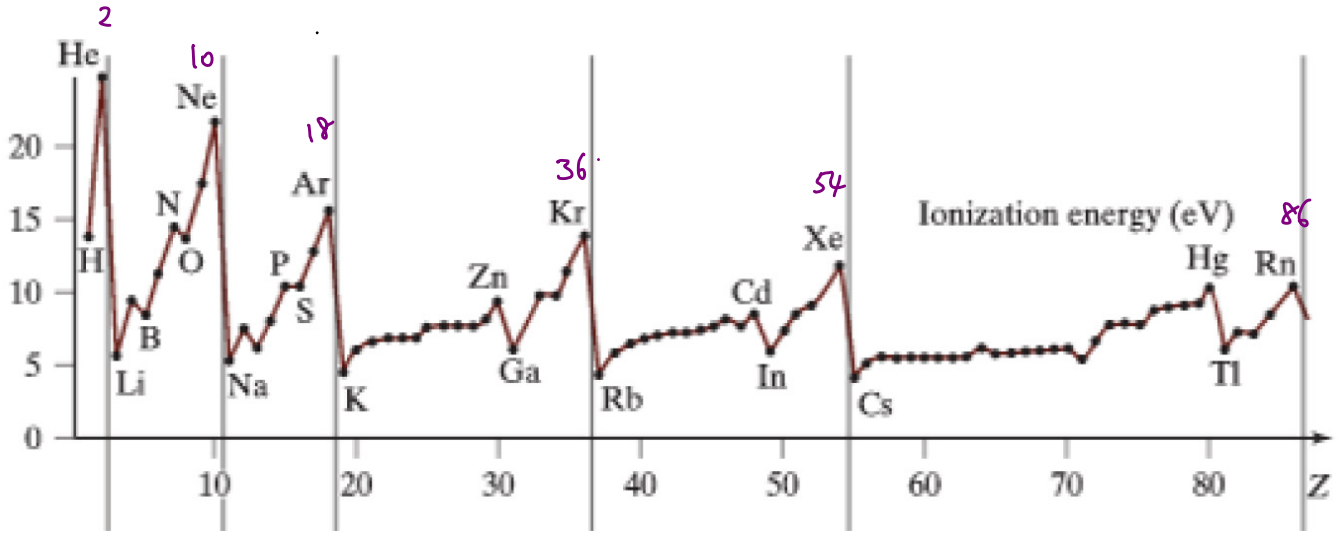
One important rule is the Pauli exclusion principle:

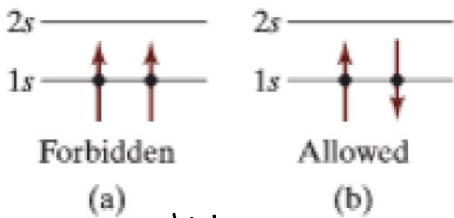**No two electrons can occupy the same quantum state**

Short reason: they are fermions and wave fun must be antisymmetric

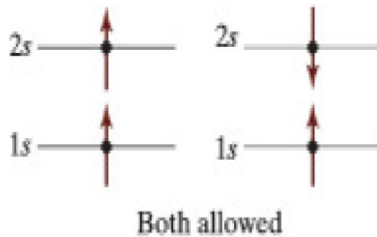$$\phi(1)\chi(2) \implies \text{antisymmetrize because fermions \& indistinguishability}$$

$$\Psi(1,2) = \phi(1)\chi(2) - \chi(1)\phi(2) \implies \begin{array}{l} \text{e.g Same state } \chi=\phi \\ \Psi_F(1,2) = \phi(1)\phi(2) - \phi(1)\phi(2) = 0! \end{array}$$

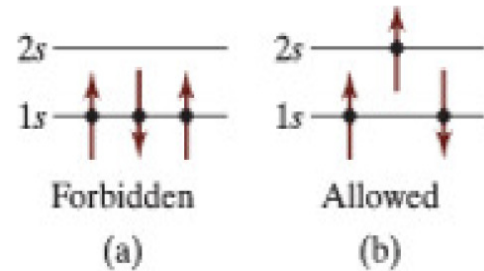$$[\text{Bosons}: \Psi_B(1,2) = \phi(1)\chi(2) + \chi(1)\phi(2)]$$

Now let's examine the consequence:

Helium

Both allowed
but correspond to excited states

$3 Li$

__ionization energy__: energy needed to remove an electron. For $_1H$: $13.6eV = E_R$

He: 1s $E_{1s} \approx -Z_{eff}^2 E_R$ Z_{eff} should be somewhere betwn 1 & 2, take $Z_{eff} \approx 1.5$

$\implies$ ionization energy $\approx (1.5)^2 \cdot E_R \approx 30.6 eV$ cf. 24.6 eV

1st   excitation energy   e.g. ── 2s ↑

[stability of atom]   1s ↑↓   ↑

High stability ⇒ low chemical activity

$\bar{E}_{2s} \approx -Z_{eff}^2 \dfrac{E_R}{2^2} \approx -\dfrac{24.6\,eV}{4}$

$= -6.15\,eV$

$\Delta E \approx -6.15 + 24.6\,eV = 18.45\,eV$

cf. 19.8 eV experiment

$_3Li$ 1e⁻ occupies 2s   2s ↑   (Hydrogen 10.2 eV)

1s ↑↓ due to Pauli principle.

2s is less tightly bound. Also $Z_{eff} = 1$ $E_2 = -\dfrac{Z_{eff}^2}{2^2} E_R$ ⇒ ionization ~ $\dfrac{13.6\,eV}{4}$

$\approx 3.65\,eV$

[chemically active] ⇐ fifth smallest ⇐ -vs. actual value $= 5.4\,eV$

due to $Z_{eff} > 1$. (not perfectly screened)

Radius ~ $\dfrac{n^2 a_B}{Z_{eff}}$ ~ $4 a_B$ larger than that for H & He

TABLE 10.1

Ionization energies and radii of the first four atoms. Atomic numbers Z are shown as subscripts on the left of chemical symbols. The energy levels are not to scale, since corresponding levels get deeper as Z increases.
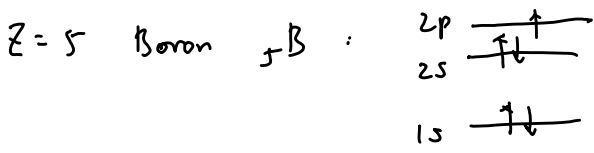
		$_1H$	$_2He$	$_3Li$	$_4Be$
Ionization energy (eV):		13.6	24.6	5.4	9.3
Radius (nm):		0.08	0.05	0.20	0.14
Occupancy of energy levels:	2s ──			↑	↑↓
	1s ↑	↑↓	↑↓	↑↓

$Z = 4$. Beryllium $_4Be$; last e⁻ in 2s ⇒ radius ~ $\dfrac{n^2 a_B}{Z_{eff}}$ $n = 2$ ⇒ radius $2 a_B$

$Z_{eff} \sim 2$ e.g. $\sqrt{2}$

⇒ more tightly bound than $_3Li$ ⇒ larger ionization energy

$E_2 \sim \dfrac{Z_{eff}^2}{n^2} E_R \gtrsim \dfrac{1}{2} E_R = 6.8\,eV$ vs. actual 9.3 eV

excitation to 2p: ~ $E_{2p} \sim -\dfrac{Z_{eff}^2}{4} E_R$ $Z_{eff} \sim 1$ $\dfrac{3.65}{eV}$

⇒ excitation energy $(-\dfrac{1}{4} - (-\dfrac{1}{2})) E_R \sim \dfrac{13.6}{4}$

vs. actual 2.7 eV

⇒ chemically active (in contrast to He)

$Z=5$ Boron $_5B$:

$2p$ ⟶↑
$2s$ ↑↓
$1s$ ↑↓

$Z=6$ to 10 still in $2p$

ionization energy ↑

radius ↓

Competitions: ① Z larger ⟹ tighter, bound ↑

② higher level

which wins? ⟶ ② for ionization ??

radius $\dfrac{n^2 a_B}{Z_{eff}} \sim \dfrac{4}{1.5\sim 2} a_B \sim (2\sim 2.6\ a_B)$?

$E_{2p} \sim -\dfrac{Z_{eff}^2}{4} E_R \sim \sim (0.56 \sim 1) E_R$

vs actual $-8.3\ eV$

↯↑↑?
N ↑↓
↑↓
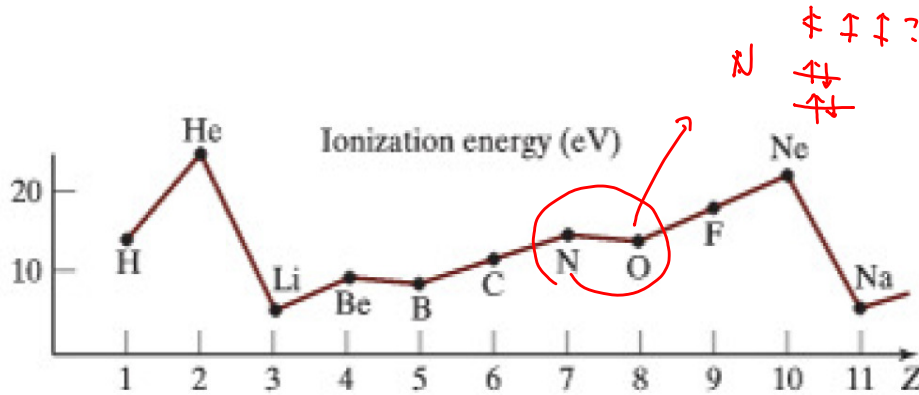
vs

↑↓↑↑
↑↓
↑↓

⟶ Coulomb repulsion decreases ionization energy

[check Hund's rules]

$_{10}$Ne : $2p$ is filled (closed shell)

$_9$F : closed shell minus one ⟹ electron affinity : attract e^- ⟹ $\bar{F}^-$

17.4 eV
large ionization energy but with large

3.4 eV

Na : electron configuration $1s^2 2s^2 2p^6 3s^1$ similar to Li : $1s^2 2s^1$
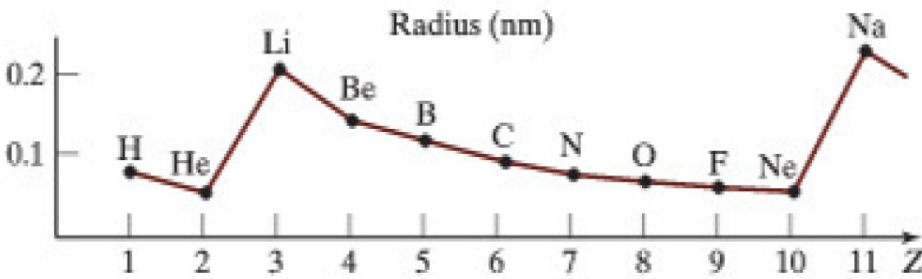
FIGURE 10.8

The ionization energies and atomic radii of the first 11 elements.

gradual change

gradual change

⟶ abrupt change when shell filled completely and new e^- is added

1s			1s
2s			2p
3s			3p
4s		3d $10 e^-$'s	4p
5s		4d	5p
6s	*	5d	6p
7s	†	6d	

$10 + 14 = 24$

*	5d	4f
†	6d	5f

Electron configurations of the ground states of the first 18 elements.

First Shell	Second Shell	Third Shell	
$_1$H : $1s^1$	$_3$Li : $1s^2 2s^1$	$_{11}$Na : $1s^2 2s^2 2p^6 3s^1$	$_{19}$K: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
$_2$He: $1s^2$	$_4$Be : $1s^2 2s^2$	$_{12}$Mg: $1s^2 2s^2 2p^6 3s^2$	
	$_5$B : $1s^2 2s^2 2p^1$	$_{13}$Al : $1s^2 2s^2 2p^6 3s^2 3p^1$	
	$_6$C : $1s^2 2s^2 2p^2$	$_{14}$S : $1s^2 2s^2 2p^6 3s^2 3p^2$	*not a*
	$_7$N : $1s^2 2s^2 2p^3$	$_{15}$P : $1s^2 2s^2 2p^6 3s^2 3p^3$	*Similarity*
	$_8$O : $1s^2 2s^2 2p^4$	$_{16}$S : $1s^2 2s^2 2p^6 3s^2 3p^4$	*betwn second & third shells*
	$_9$F : $1s^2 2s^2 2p^5$	$_{17}$Cl : $1s^2 2s^2 2p^6 3s^2 3p^5$	
	$_{10}$Ne: $1s^2 2s^2 2p^6$	$_{18}$Ar : $1s^2 2s^2 2p^6 3s^2 3p^6$	[see above schematic table ↑]

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Periodic table

d can accommodate 10 e⁻'s

→ involve f levels !

- Transition metal
  3d, 4d, 5d, 6d, ...

- Even though 3d
  Ras higher energy,
  4s is further
  out, can interact
  w.
  other atoms
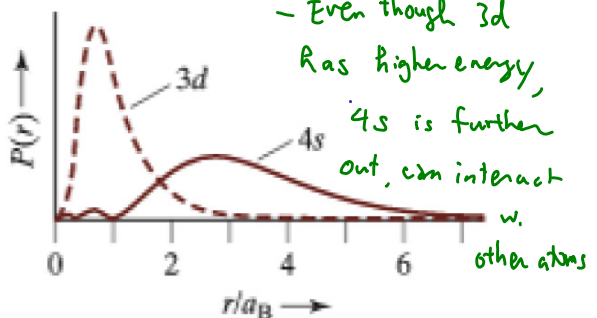
- Prediction of physical properties: total
  Spin S, total orbital angular momentum L
  and total angular momentum J ?
  $^{25th}L_J$ $L = 0, 1, 2, 3, ..$
                                    S P D F ...

  ✳ filled levels : $\Sigma S = 0$, $\Sigma L = 0$ Ne: $^1S_0$
  (closed shell/subshell ⟹ $S = 0 = L$ ⟹ $J = 0$)
  ✳ closed + 1 : $L = 0$, $S = \frac{1}{2}$, $J = \frac{1}{2}$ Na: $^2S_{1/2}$
                                                         F: $^2P_{3/2}$
  ✳ closed − 1 : $L = \ell_{last}^{-1}$, $s = \frac{1}{2}$, $J = \ell + \frac{1}{2}$

H

Intermediate

Nonmetals

Metals

Metals